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## The Formation of $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and BaFe<sub>12</sub>O<sub>19</sub> in the Presence of Iron (II) Hydroxide and Nitrates with or without Ba (II)

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Alkaline suspensions containing 0.45M FeCl<sub>2</sub> and different concentrations of excess NaOH and of NaNO<sub>3</sub> were subjected to autoclaving between 150 and 250°C. Disklike  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles were formed with or without the formation of isotropic Fe<sub>3</sub>O<sub>4</sub> ones above 180°C. Ferromagnetic platelike BaFe<sub>12</sub>O<sub>19</sub> particles were also formed in the presence of Ba(II) and Fe(II) with the 1:8 atomic ratio under the conditions similar to those for the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> formation. The magnetic properties of the BaFe<sub>12</sub>O<sub>19</sub> sample were investigated at room temperature.

KEY WORDS : Fe(OH)<sub>2</sub> /  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> / BaFe<sub>12</sub>O<sub>19</sub> / Ferromagnetic precipitate / Coercivity / Autoclaving / Alkaline suspension

### Introduction

It is known that platelike particles of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> can be formed by autoclaving of alkaline suspension of iron (III) species, such as  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>,<sup>1)</sup> iron (III) hydroxide<sup>2)</sup> or  $\alpha$ -FeO(OH) at temperatures above 160°C.<sup>3)</sup> It is also known that a ferromagnetic precipitate of BaFe<sub>12</sub>O<sub>19</sub> can be prepared in the presence of Ba(OH)<sub>2</sub> and either iron (III) hydroxide or  $\alpha$ -FeO(OH) with the 1:8 atomic ratio under the conditions where the transformation into  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> proceeded.<sup>4,5)</sup> It was reported that the aging of Fe(OH)<sub>2</sub> suspensions containing nitrates at 90°C gave Fe<sub>3</sub>O<sub>4</sub> particles with or without formation of  $\alpha$ -FeO(OH) ones, no  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> having been obtained.<sup>6)</sup>

We have found that the addition of nitrates enables the use of Fe(II) as the source of platelike  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and ferromagnetic BaFe<sub>12</sub>O<sub>19</sub> particles. This paper describes the conditions for the formation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> by autoclaving Fe(OH)<sub>2</sub> and also for the formation of BaFe<sub>12</sub>O<sub>19</sub> from Fe(II) and Ba(II), both in the presence of nitrates. The magnetic properties of BaFe<sub>12</sub>O<sub>19</sub> at room temperature for the samples in this work are also reported.

### Experimental

An acidic solution was prepared in a 1 dm<sup>3</sup> autoclave made of stainless steel, by mixing aqueous solutions of NaNO<sub>3</sub> and FeCl<sub>2</sub> (each of reagent grade). To this a NaOH solution was added and each resulting suspension was diluted with conductivity water to 0.7 dm<sup>3</sup>. A number of alkaline suspensions of Fe(OH)<sub>2</sub>, each containing 0.45M (M = mol/dm<sup>3</sup>) Fe(II), were prepared by varying the concentrations of excess NaOH and nitrates. They were heated to

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the desired temperatures at a rate of  $3^{\circ}\text{C min}^{-1}$ , kept at 150, 180, 200, 230, or  $250^{\circ}\text{C}$  with mechanical stirring at 550 rpm for a fixed time of 2h and then allowed to cool to room temperature. The resulting products were separated by filtration, well washed with water, and then dried at  $80^{\circ}\text{C}$  in air.

Acidic solutions containing Fe(II) and Ba(II) with the 8:1 atomic ratio were prepared by dissolving  $\text{BaCl}_2$  in the acidic solutions mentioned above. Alkaline suspensions were prepared and subjected to autoclaving under the conditions similar to those described above. The ferromagnetic suspensions were treated with 1M HCl until the pH decreased to 2 to remove remaining Ba(II) as a carbonate, which was formed with carbon dioxide from the atmosphere, before the separation by filtration.

The products were subjected to examinations by X-ray diffraction using  $\text{FeK}\alpha$  radiation (XRD), scanning electron microscopic observation (SEM), and to the BET surface area measurement using nitrogen. The  $\text{Fe}_3\text{O}_4$  and  $\alpha\text{-Fe}_2\text{O}_3$  contents in the products prepared in the absence of Ba(II) were determined by comparing the relative intensities of XRD peaks of  $\text{Fe}_3\text{O}_4$  d(311) 2.53 and  $\alpha\text{-Fe}_2\text{O}_3$  d(104) 2.69Å. Magnetic measurements on the ferromagnetic samples, which had been packed with 1.2–2.0 in packing densities, were carried out at room temperature in a magnetic field up to 10 kOe ( $1 \text{ kOe} = 10^6/4 \pi \text{ Am}^{-1}$ ), by using a vibrating-sample magnetometer.

### Results and Discussion

The starting, alkaline suspensions containing 0.45M  $\text{FeCl}_2$ , 0.15M  $\text{NaNO}_3$  and different amounts of excess NaOH were subjected to autoclaving at temperatures between 150 and  $250^{\circ}\text{C}$ .  $\text{Fe}_3\text{O}_4$  was formed with  $\alpha\text{-FeO(OH)}$  at  $150^{\circ}\text{C}$ , whereas  $\alpha\text{-Fe}_2\text{O}_3$  was formed with or without  $\text{Fe}_3\text{O}_4$  at temperatures above  $180^{\circ}\text{C}$  depending on the concentration of excess NaOH and temperature. The typical iron oxide samples prepared under the various conditions are given in Table 1. The shape of  $\alpha\text{-Fe}_2\text{O}_3$  particles formed depended on the concentration of excess NaOH (Fig. 1).

Table 1. Products Obtained by Autoclaving at Different Temperatures, T, Alkaline Suspensions Containing 0.45M  $\text{Fe(OH)}_2$ , 0.15M  $\text{NaNO}_3$  and Either 0.3 or 6.0M Excess NaOH.

Sample	NaOH/M	T/ $^{\circ}\text{C}$	Contents	
			$\alpha\text{-Fe}_2\text{O}_3$	$\text{Fe}_3\text{O}_4$
A*	0.3	180	0	0.83
B	6.0	180	0.19	0.81
C	0.3	200	0.28	0.72
D	6.0	200	1.0	0
E	0.3	230	0.37	0.63
F	0.3	250	1.0	0

\* Consisted of  $\alpha\text{-FeO(OH)}$  in place of  $\alpha\text{-Fe}_2\text{O}_3$

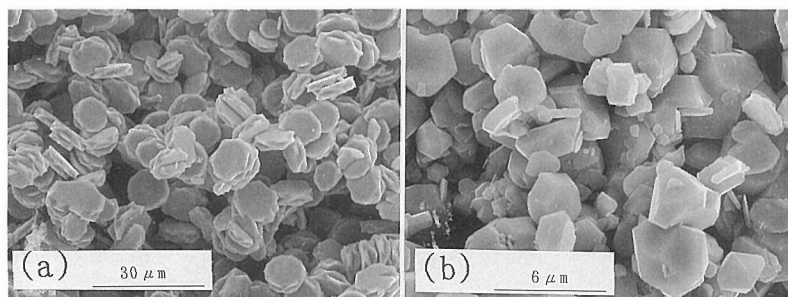


Fig. 1. SEM photographs of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> samples D(a) and F(b).

In order to investigate the effect of the concentration of the nitrates on the formation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> under the conditions for the formation of Fe<sub>3</sub>O<sub>4</sub> with  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, the alkaline suspensions containing 0.9M NaNO<sub>3</sub>, 0.45M FeCl<sub>2</sub>, and different concentrations of excess NaOH were subjected to autoclaving at temperatures above 180°C. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> content in the products remarkably increased with increasing the concentrations of NaNO<sub>3</sub> and excess NaOH. In these experiments, the nitrate concentration required for the formation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> decreased with increases in the temperature and the concentration of excess NaOH. For instance,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was formed without the formation of Fe<sub>3</sub>O<sub>4</sub> at 180°C in the presence of 0.9M NaNO<sub>3</sub> and 6M excess NaOH, and at 250°C in the presence of 0.08M NaNO<sub>3</sub> and 0.3M excess NaOH (Fig. 2).

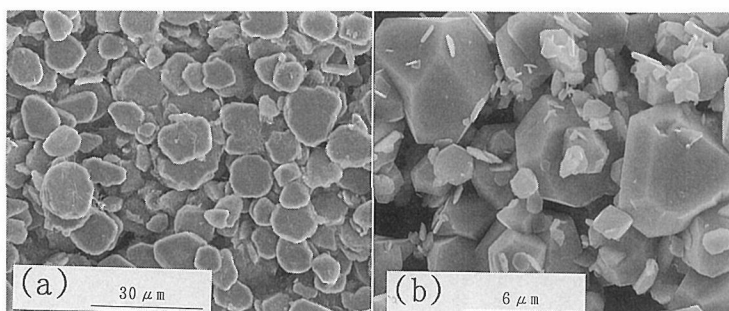


Fig. 2. SEM photographs of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> samples prepared at 180°C in the presence of 0.9M NaNO<sub>3</sub> and 6M NaOH (a), and at 250°C in the presence of 0.08M NaNO<sub>3</sub> and 0.3M NaOH (b).

The starting, alkaline suspensions containing 0.45M FeCl<sub>2</sub>, 0.056M BaCl<sub>2</sub>, 0.15M NaNO<sub>3</sub>, and different concentrations of excess NaOH were subjected to autoclaving at 200, 250 or 300°C. Ferromagnetic, brownish precipitates, consisting of BaFe<sub>12</sub>O<sub>19</sub> with or without  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, were formed at temperatures above 200°C, depending on the concentration of excess NaOH. The properties of typical BaFe<sub>12</sub>O<sub>19</sub> samples found by XRD to consist only of

BaFe<sub>12</sub>O<sub>19</sub> are given in Table 2. The values of magnetization at 10 kOe, M, ( $1 \text{ emu/g} = 4 \pi \rho \cdot 10^{-4} \text{ T}$ , where  $\rho = 5.3$  is specific gravity), depend on the conditions for their formation,

Table 2. Properties of the Typical BaFe<sub>12</sub>O<sub>19</sub> Sample Prepared by Autoclaving at Different Temperatures, T, of Aqueous Suspensions Containing 0.45M FeCl<sub>2</sub>, 0.15M NaNO<sub>3</sub>, 0.056M Ba(OH)<sub>2</sub> and Different Concentrations of Excess NaOH.

Sample	Excess NaOH/M	T/°C	M/emu g <sup>-1</sup>	Hc/kOe	S/m <sup>2</sup> g <sup>-1</sup>
G	6.0	300	47	0.8	3.6
H	1.0	300	34	0.7	1.5
I	6.0	250	33	0.8	3.9
J	2.0	250	30	0.8	1.0
K	1.0	250	30	0.7	0.7
L	6.0	200	20	0.7	9.5

whereas the values of coercive force, Hc, are lower than those of the ones prepared in the presence of Fe (III) and depend slightly on the conditions. These BaFe<sub>12</sub>O<sub>19</sub> samples were found by SEM to consist of hexagonal, platelike particles whose diameter was greater than those of the ones prepared in the presence of iron (III) and became small with increasing the concentration of excess NaOH at 0.056M Ba(II) (Fig. 3). Such low Hc values might have resulted from the extremely large sectional-shape anisotropy of each particle.

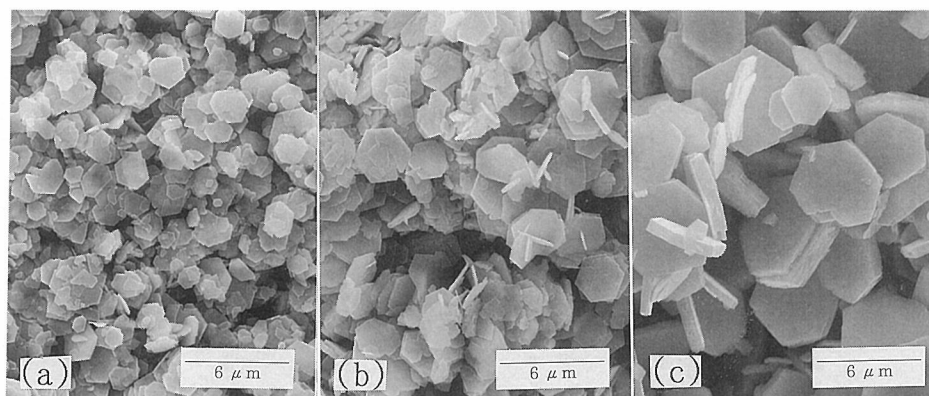


Fig. 3. SEM photographs of the BaFe<sub>12</sub>O<sub>19</sub> samples G (a), I (b) and J (c).

In order to investigate the effects of the concentration of the total nitrates on the formation of BaFe<sub>12</sub>O<sub>19</sub>, suspensions containing 1.0M NaNO<sub>3</sub>, 0.45M FeCl<sub>2</sub>, 0.056M BaCl<sub>2</sub>, and 6M excess NaOH were prepared and subjected to autoclaving at 250°C. The BaFe<sub>12</sub>O<sub>19</sub> content in the products and their magnetic properties did not depend strongly on the nitrate concentration.

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